353. *Catalytic Approaches to Complex Compounds of Rhodium*(III)

By R. D. Gillard, J. A. Osborn, and G. Wilkinson

Convenient rapid preparations of a number of compounds of rhodium(III) with nitrogen ligands such as pyridine, 2,2′-bipyridyl, and dioximes, are described, involving the use of catalytic amounts of reducing agents. Catalyses of nucleophilic replacements of chloride ion in several halogenoammine complexes are also demonstrated. Some reactions of *trans*-dichlorotetrapyridinerhodium(III) chloride have been studied, and certain claims in the literature are revised. Spectroscopic studies of complexes of rhodium(III) with dioximes are presented, leading to reformulation of some complex acids.

The study of the co-ordination chemistry of rhodium has been hampered by the slow and often inconvenient preparative methods required, and by the inert nature of the complexes formed. We present here some syntheses of rhodium complexes which are extremely convenient and quickly performed.

Ethanol, and several other alcohols, catalyse[1] the formation of *trans*-dichlorotetrapyridinerhodium(III) cation. A similar effect was remarked[2] in the synthesis of malonato- and diethyldithiocarbamato-complexes of rhodium(III). Other reasonably rapid preparations of rhodium(III) species in the literature (*e.g.*, $[Rh(bipy)_2Cl_2]^+$ and $[Rh(DMGH)_2Cl_2]^-$) * have involved ethanol as a solvent for the ligand, but we find that, in fact, it also acts as a catalyst, in that such reactions are not practicable in the absence of ethanol. Recently,[3,4] *trans*-dihalogenotetrapyridinerhodium(III) salts have been most readily prepared by using hypophosphorous acid as a catalyst. We and others[5] have observed the increase in the rate of nucleophilic substitution in the *trans*-dichlorobisethylenediaminerhodium(III) cation in the presence of hypophosphorous acid, hydrazinium chloride, or sodium borohydride (even in the cold). The catalytic effect of ethanol in the synthesis of $[Rh\ py_4Cl_2]Cl$ has very recently been studied kinetically.[6]

These catalytic reagents are not only typical reducing agents but also those which give rise to complex metal hydrides.[7] We have previously[8] observed the catalysis of the isomerism

$$trans\text{-}[Co\ en_2Cl_2]^+ \longrightarrow cis\text{-}[Co\ en_2Cl_2]^+$$

---

* Abbreviations used for ligands are: bipy, 2,2′-bipyridyl; $DMGH_2$, dimethylglyoxime; en, ethylenediamine; *o*-phen, 1,10-phenanthroline; pn, diamino-1,2-propane; and py, pyridine.

[1] M. Delépine, *Compt. rend.*, 1953, **236**, 559.
[2] C. K. Jørgensen, Cyanamid European Research Institute, Technical Report, T.I.C. P8, 1960.
[3] B. N. Figgis, R. D. Gillard, R. S. Nyholm, and G. Wilkinson, *J.*, 1964, 5189.
[4] J. A. Osborn, R. D. Gillard, and G. Wilkinson, *J.*, 1964, 3168.
[5] F. Basolo, E. J. Bounsall, and A. J. Poë, *Proc. Chem. Soc.*, 1963, 366.
[6] J. V. Rund, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1964, **3**, 658.
[7] J. Chatt, *Proc. Chem. Soc.*, 1962, 318.
[8] R. D. Gillard and G. Wilkinson, *J.*, 1963, 3594.

by borohydride ion and now find that it is effected only by such hydride-producing agents as hypophosphorous acid, hydrazinium chloride, formic acid, and zinc amalgam while other reducing agents such as sulphite, nitrite, or quinol give rise to immediate formation of cobalt(II). It was suggested that the isomerism occurs through the monohydridic intermediate and it seems possible that the hydride-forming reagents can initiate a different mechanistic course in certain substitutions, often with an apparent rate increase. They may also give rise to products inaccessible by the usual substitution methods. We suggest that this catalysis arises from the ease of formation of the hydridic intermediates relative to that of the usual aquo-intermediate. Further substitution in the position *trans* to the hydride ion is then rapid. We have therefore investigated the possibility of synthesising rhodium complexes by hydride catalysis under conditions where the hydride formed is likely to be only transient. We have approached such syntheses from two directions, *viz.*,

$$\mathrm{RhX_6}^{2-} + \mathrm{L} \xrightarrow{\mathrm{H}^-} [\mathrm{RhL_4X_2}]^+ \xleftarrow{\mathrm{H}^-} [\mathrm{RhL_4Cl_2}]^+ + 2\mathrm{X}^-$$

Preparations of some ammine and related complexes of rhodium by these methods are discussed below.

(a) trans-*Dihalogenotetrapyridinerhodium*(III) *Salts.*—By refluxing hydrated rhodium trichloride with aqueous pyridine in excess using alcohols as catalysts, Delépine [1] obtained *trans*-[Rh $\mathrm{py_4Cl_2}$]Cl,$6\mathrm{H_2O}$. We have previously shown [9] that hot solutions of this kind in the absence of catalysts contain trichlorotrispyridinerhodium(III) only and now find that a complete conversion into the tetrapyridine compound is catalysed by hypophosphorous acid, sodium hypophosphite, or hydrazinium chloride when a small amount is added to the hot solutions. Sodium borohydride or zinc amalgam catalytically convert such solutions to the *trans*-[Rh $\mathrm{py_4Cl_2}]^+$ cation in the cold. Care must be exercised with the preparation using borohydride since an excess of the reagent will attack the required product. However, gentle warming of the resultant solution gives a good yield of the required product. In a mixture of ethanol and 2-methoxyethanol, hydrated rhodium trichloride and pyridine form *trans*-[Rh $\mathrm{py_4Cl_2}$]Cl immediately on reaching ebullition. The product is precipitated by adding ether, and is recrystallised from water in extremely good yield. When an aqueous solution of rhodium trichloride containing pyridine is treated with a little hydridodichlorotris(triphenylphosphine)iridium(III), dissolved in acetone or pyridine as hydride-transfer agent, and the resulting solution warmed to 55°, the [Rh $\mathrm{py_4Cl_2}]^+$ cation is rapidly formed in solution, and can be obtained as shiny yellow feathery crystals of its chloride pentahydrate on cooling and standing.

Preparations using hypophosphorous acid have previously been recorded [3,4] for the cations *trans*-[Rh $\mathrm{py_4X_2}]^+$ from $[\mathrm{RhX_6}]^{3-}$ and excess of pyridine (X = Br or I). However, on boiling a solution of *trans*-[Rh $\mathrm{py_4Cl_2}$]Cl with an excess of potassium bromide in the presence of hypophosphorous acid, the solution darkens and suddenly precipitates a very insoluble fawn compound. This is [Rh $\mathrm{py_4Br_2}$][Rh $\mathrm{py_2Br_4}$] which was obtained by Poulenc [10] by boiling [Rh $\mathrm{py_4Br_2}$]Br with concentrated hydrobromic acid, and by us [3] using hypophosphorous acid. On heating a solution of *trans*-[Rh $\mathrm{py_4Cl_2}$]Cl in the presence of an excess of potassium iodide with a little hypophosphorous acid, halide exchange is again catalysed, since [Rh $\mathrm{py_4I_2}]^+$ cation is formed rapidly in solution; however, the solution soon precipitates dark brown tri-iodotripyridinerhodium(III), the di-iodo cation being stable only in the presence of excess of pyridine.

(b) *Thiocyanato-complexes.*—The reaction of $[\mathrm{Rh(SCN)_6}]^{3-}$ with pyridine has previously been investigated.[11] The product after refluxing was described as trithiocyanatotripyridinerhodium(III); this product we find to be the nearly pure orange isomer described below, though there is always a small amount of the pale yellow isomer present, which can be removed by recrystallising from dichloromethane. If a drop of hypophosphorous acid

[9] R. D. Gillard and G. Wilkinson, *J.*, 1964, 1224.

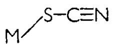
[10] P. Poulenc, *Ann. chim. France*, 1935, **4**, 632.

[11] J. Meyer and H. Kienitz, *Z. anorg. Chem.*, 1939, **242**, 281.

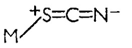
is added to the reaction mixture, the cation [Rh $py_4(SCN)_2]^+$ is not formed. The product is again a mixture of the two isomers, containing appreciably more of the pale yellow one. These isomers [both having the stoicheiometry Rh $py_3(SCN)_3$] can be separated by their differing solubilities in dichloromethane, the orange isomer being very soluble, the pale yellow isomer virtually insoluble; it can, however, be recrystallised from aqueous pyridine.

The electronic spectra of both yellow and orange isomers show bands around 375 mμ, supporting S-bonded rather than N-bonded thiocyanate. By comparison with the analogous formation of the isomers of trihalogenotripyridinerhodium(III) from the hexachlororhodate(III) or hexabromorhodate(III) ions, where the major products (85%) are the 1,2,6-isomers, we tentatively assign 1,2,6-structure to orange [Rh $py_3(SCN)_3$] and 1,2,3-structure to yellow [$Rh(py)_3(SCN)_3$]. Properties which distinguish between the isomers are given in Table 1.

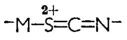
In both isomers absorption occurs in the infrared spectrum at about 840 $cm.^{-1}$, the orange isomer showing one band, and the pale yellow isomer three in this region, which has been said [12] to indicate N-bonded thiocyanate *in complexes of the type* $[M(NCS)_6]^{3-}$. Since there appears to be no doubt that the hexathiocyanatorhodate(III) ion contains S-bonded thiocyanate, there would have to be a complete rearrangement during the reaction with pyridine if N-bonded thiocyanate were present in either isomer of [Rh $py_3(SCN)_3$]. Such a rearrangement is unlikely, so we prefer to assign the bands at 840 $cm.^{-1}$ to overtones of the NCS bending vibrations; it often occurs [13] that such overtones are as intense as their fundamentals. No absorption was apparent in either isomer between the pyridine bands at 700 and 750 $cm.^{-1}$, even when mulls in carbon disulphide were examined (to avoid the paraffinic absorption at 720 $cm.^{-1}$). However, the intense band around 700 $cm.^{-1}$ due to pyridine may well obscure the weak C–S absorption due to the co-ordinated SCN^-. There is, of course, the further possibility that, of the possible forms of sulphur-co-ordinated thiocyanate shown, the normally favoured (*a*) no longer predominates in these tripyridine compounds, because of modification of the *d*-orbitals of the rhodium by the co-ordinated pyridine.



(a)



(b)



(c)

The formation of only tripyridine complexes in the thiocyanate system is reminiscent of the reaction of dichlorotetrapyridinerhodium(III) chloride with iodide ion; either with or without added hypophosphorous acid, the product is tri-iodotripyridinerhodium(III), the tetrapyridine species [Rh $py_4I_2]^+$ being stable only when excess of pyridine is present. It has been pointed out [14] that in the *trans*-dichlorotetrapyridinecobalt(III) cation, the molecules of pyridine must adopt a twisted configuration about the Co–N bond, the whole ion resembling a four-bladed propeller. The *trans*-dichlorobisbipyridylcobalt(III) cation is, so far as the four nitrogen atoms and the rings are concerned, however, genuinely planar. In view of the existence of the $[Rh(bipy)_2I_2]^+$ cation, we feel that the instability of [Rh $py_4X_2]^+$, where X = I^- or SCN^- may be due to steric factors arising from compression of the propeller in the *xy*-plane about the metal by the large axial ligands.

(c) *Other reactions of* trans-[Rh py_4Cl_2]Cl.—*trans*-Dichlorotetrapyridinerhodium(III) chloride is a useful compound with some interesting reactions. On warming with aqueous potassium cyanide, pyridine is lost, and a compound with the empirical formula Rh $py_2(CN)_2Cl,2H_2O$ is formed as a white precipitate. The infrared spectrum reveals that it contains both terminal (ν = 2152 $cm.^{-1}$) and bridging (ν = 2201 $cm.^{-1}$) cyanide groups, and in view of this and its insolubility in water, pyridine and other solvents, it is probably polymeric.

When *trans*-[Rh py_4Cl_2]Cl is heated with aqueous ammonia on a steam-bath, pyridine

---

[12] J. Lewis, R. S. Nyholm, and P. W. Smith, *J.*, 1961, 4590.

[13] L. Jones, *J. Chem. Phys.*, 1958, **28**, 1234.

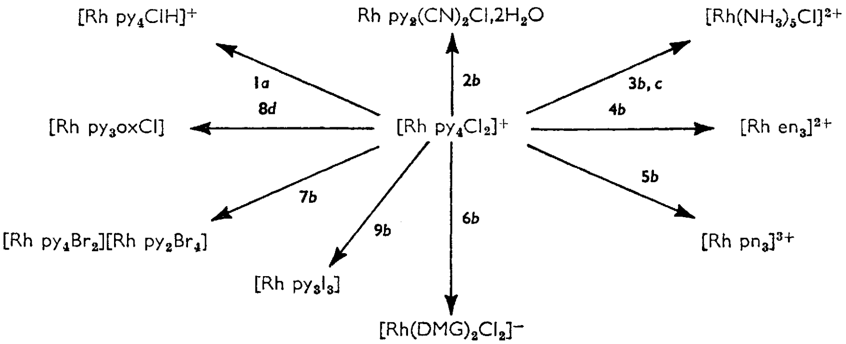
[14] F. Basolo and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 2676.

is again lost, and chloropentamminerhodium(III) chloride crystallises out in excellent yield; this reaction was described by Jørgensen.[15] We have also confirmed the reaction [16] of [Rh py_4Cl_2]Cl with warm potassium oxalate in aqueous solution to give the non-electrolyte chloro-oxalatotripyridinerhodium(III). This is very slightly soluble in pyridine, and its infrared spectrum shows bands characteristic of co-ordinated oxalate at 1702 and 1671 $cm.^{-1}$. A similar reaction [10] occurs with *trans*-[Rh $py_4Br_2]^+$ to give [Rh py_3oxBr].

It has been claimed [11] that when *trans*-[Rh py_4Cl_2]Cl is heated with ethylenediamine, chloropyridinebisethylenediaminerhodium(III) chloride is formed; we have found that this is not so. The product is, in fact, trisethylenediaminerhodium(III) chloride. This is not surprising in view of the displacement of pyridine by ammonia mentioned earlier. An entirely analogous reaction occurs with propylenediamine, the product being trispropylenediaminerhodium(III) chloride.

There is a report [17] that, when *trans*-[Rh py_4Cl]Cl in aqueous solution is refluxed for 36 hours with dimethylglyoxime, the product is *trans*-chloropyridinebisdimethylglyoximatorhodium(III) (X). This has been found not to be so; the product is a mixture of the yellow-orange 1,2,3-trichlorotripyridinerhodium(III) and a few pale yellow crystals (~5%) which contain rhodium, chlorine, and pyridine, but no dimethylglyoxime. The reactants *trans*-[Rh py_4Cl_2]Cl (A) and dimethylglyoxime (B) do not give X under any conditions; by treating a warm ethanolic solution of A and B in the molar ratio 1 : 1, with or without the addition of a little sodium borohydride, rapid reaction ensures, pyridine is evolved, and the salt *trans*-[Rh $py_4Cl_2]^+$ *trans*-$[Rh(DMGH)_2Cl_2]^-$ is produced, identified by analysis and comparison of spectra with an authentic sample, prepared by double decomposition. If the mole ratio $A : B = 1 : 2$, the product is pyridinium *trans*-dichlorobisdimethylglyoximatorhodate(III), originally described by Dwyer and Nyholm.[18] It is not unexpected that two dimethylglyoxime radicals should displace all four pyridine molecules in the plane. The catalysed substitution of chloride ion by pyridine in the *trans*-dichlorobisdimethylglyoximatorhodate(III) ion, to give X, is discussed later. Reactions of *trans*-[Rh $py_4Cl_2]^+$ are summarised in Scheme 1.

Scheme 1



Conditions: 1, BH_4^-; 2, CN^-; 3, NH_3; 4, en; 5, pn; 6, DMG; 7, Br^-, H_3PO_2; 8, ox^-; 9, I^-.
References: *a*, ref. 4; *b*, this work; *c*, ref. 15; *d*, ref. 16.

(d) trans-*Dichlorobisbipyridylrhodium*(III) *Salts*.—Numerous attempts have been made [19] to prepare pure salts of the $[Rh(bipy)_2Cl_2]^+$ cation; products described in the literature are notoriously difficult to separate from other reaction products. In these early preparations, alcohol was used as solvent for the bipyridyl, and we attribute the formation of small amounts of $[Rh(bipy)_2Cl_2]^+$ in these cases mainly to the catalytic effect of this

---

[15] S. M. Jørgensen, *J. prakt. Chem.*, 1885, **25**, 478.
[16] L. Tchugaev, *Bull. Soc. chim.*, 1919, **25**, 234.
[17] V. V. Lebendenski and I. A. Federov, *Ann. sect. Platine*, 1948, **22**, 158.
[18] F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 266.
[19] F. M. Jaeger and J. A. Van Dijk, *Kon. Ned. Acad. wet., Amsterdam*, 1934, **37**, 284.

alcohol. When acetone is used to dissolve the bipyridyl, the bisbipyridyl complex is formed only very slowly, in extremely low yield. However, on addition of a few drops of ethanol, the $[Rh(bipy)_2Cl_2]^+$ cation begins to appear rapidly in solution. In a more recent preparation,[20] using the fusion of hydrated rhodium trichloride with bipyridyl, the bulk product is impure trisbipyridylrhodium(III) chloride. The bisbipyridyl compound, which is a by-product, is recovered as its slightly soluble nitrate. Recent interest in these complexes arises from the observation [21] that rhodium trichloride in methanol which contains bipyridyl gives a purple colour on shaking with zinc amalgam. This was later found [22] to be due to a reduction of the required bipyridyl complex and oxidation of such purple solutions in the presence of chloride ion might be expected to give rise to the $[Rh(bipy)_2Cl_2]^+$ cation. Although dark yellow solutions are obtained in this way, they do not contain the desired salt. However, several other catalysed processes give rise to the dichlorobisbipyridylrhodium(III) cation. When hydrated rhodium trichloride is dissolved in a 1 : 1-ethanol–2-methoxyethanol mixture, bipyridyl dissolved in ethanol added, and the mixture slowly brought to the boil, $[Rh(bipy)_2Cl_2]Cl$ is precipitated as a bright yellow powder. Its solution in hot water when treated with sodium nitrate or perchlorate gives the required salts as pale yellow crystals. Yields are high, the loss being incurred during recrystallisation. Interestingly enough, when an aqueous alcoholic solution of rhodium trichloride and bipyridyl is treated with a little hypophosphorous acid and allowed to stand in the cold, yellow needles of $[Rh(bipy)_2Cl_2]Cl,2H_2O$ crystallise out over a few days. However, the preferred method is to add a small quantity of hydrazinium chloride to a hot ethanolic solution of rhodium trichloride and bipyridyl, when there is an extremely rapid colour change and on cooling beautiful crystals of $[Rh(bipy)_2Cl_2]Cl,2H_2O$ are obtained. The identity of our products with those prepared by literature methods has been shown by electronic and infrared spectra.

Although hypophosphorous acid slowly gives the required compound in the cold, when the solutions are boiled the product is contaminated by phosphorus-containing products. If molar amounts of hypophosphorous acid are added to boiling mixtures of rhodium trichloride and bipyridyl in aqueous ethanol a yellow, highly insoluble product is obtained. It contains phosphorus and its infrared spectrum shows modes due to P–H (*ca.* 2350 cm.$^{-1}$) and P–O (*ca.* 890 cm.$^{-1}$) as well as the characteristic bonded bipyridyl frequencies. It appears that this is a hypophosphite complex; no chlorine was present. More interesting, however, was the behaviour of the complex in aqueous solution. Insoluble in cold water, it dissolves in hot water to give a dark brown solution which, if cooled rapidly, shows a high-field line in the proton-resonance spectrum characteristic of hydrogen bonded to rhodium directly. On cooling, the solution gradually lightens to a pale yellow from which the original complex can be recovered. This cycle can be performed many times with only a gradual loss in efficiency. It is relevant that the same cycle can be initiated by treating $[Rh\ bipy_2Cl_2]Cl$ in aqueous solution with sodium hypophosphite.

We have assigned *trans*-stereochemistry to the rhodium(III) bisbipyridyl cations from a consideration of their electronic spectra in aqueous solution. These have not been previously reported and are recorded in the Experimental section. Previous assignments of stereochemistry were based firstly [22] on the splitting of the in-phase out-of-plane CH vibrations of the bipyridyl, allegedly due to the *cis*-configuration, and later on the formation [23] of an adduct with hydrogen chloride, indicating the *trans*-configuration.

(e) trans-*Dichlorobis*-1,10-*phenanthrolinerhodium*(III) *Chloride*.—This salt is new. The preparation is analogous to that of the bipyridyl derivative; the hydrazine-catalysed reaction is again the simplest, and gives a very good yield. Salts vary from bright to pale

---

[20] B. Martin and G. M. Waind, *J.*, 1958, 4284.

[21] F. P. Dwyer, unpublished work, quoted in W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, 1954, **54**, 959.

[22] B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207.

[23] R. D. Gillard and G. Wilkinson, *J.*, 1964, 1640.

yellow; spectroscopic data are recorded in the Experimental section. Again if hypophosphorous acid is used in molar quantities in hot aqueous ethanolic solutions of rhodium trichloride and 1,10-phenanthroline a hypophosphite complex is formed entirely analogous to that described in the previous section. Again *trans*-stereochemistry has been assigned to this compound because of the similarity of its electronic spectra to that of the *trans*-bisbipyridyl complex.

(f) *Other Bisbipyridylrhodium*(III) *Compounds*.—Related compounds containing the bisbipyridylrhodium(III) moiety can be prepared by similar methods; when hexabromorhodate(III) ion is allowed to react with bipyridyl in aqueous ethanol a fawn precipitate is given on heating. This contains co-ordinated bipyridyl and analysis yields the empirical formula Rh_2dipy_3Br. This compound is insoluble in dichloromethane but soluble in boiling hydrobromic acid or after prolonged boiling with water. It can be recovered unchanged from hydrobromic acid but gives a yellow solution in hot water, suggesting that hydrolysis has taken place. If hydrazinium chloride is added to the hot bipyridyl–hexabromorhodate reaction mixture, a little fawn precipitate is given but on cooling and standing beautiful plate-like orange crystals grow in the solution. These are $[Rh\,bipy_2Br_2]Br,2H_2O$. The replacement of chloride in $[Rh\,bipy_2Cl_2]^+$ cation by bromide even in the presence of hydridic catalysts is slow and the above synthesis is the most convenient. This is not so in the case of $[Rh\,bipy_2I_2]^+$ cation. There is fairly ready replacement of the chloride in $[Rh\,bipy_2Cl_2]^+Cl$ with excess of iodide present in solution, and the rate of this replacement is increased by catalysis, especially by hypophosphorous acid. $[Rh\,bipy_2I_2]I^-$ is sparingly soluble in water and comes out of solution as a brick-red precipitate. If bipyridyl in ethanol is added to a hot solution of $[RhI_6]^{3-}$ anion, a black precipitate is found, which cannot be substituted further, presumably because of its extreme insolubility. Analyses were inconclusive. In attempts to prepare the bisthiocyanatobispyridylrhodium(III) cation by either of the possible routes, both catalysed and uncatalysed, a red compound is formed, usually as an oil, which we have been unable to characterise.

(g) *Complexes of Rhodium*(III) *with Ethylenediamine*.—Earlier preparations of trisdiaminerhodium(III) salts utilised the slow reaction of the diamine with rhodium tri-iodide. However, when an excess of ethylenediamine is added to a warm alcoholic solution of rhodium trichloride trihydrate, $[Rh\,en_3]Cl_3$ precipitates immediately. Propylenediamine behaves identically. Yields of these reactions are virtually quantitative. We have been unable to make complexes containing the bisethylenediaminerhodium(III) moiety catalytically. However, the rate of nucleophilic substitution by bromide and iodide in the *trans*-dichlorobisethylenediaminerhodium(III) cation is enormously enhanced by catalytic amounts of hydridic reagents such as sodium borohydride or hypophosphite.

(h) *Rhodium Complexes with Dimethylglyoxime*.—Several complexes of rhodium(III) with dimethylglyoxime have been reported. The dichlorobisdimethylglyoximatorhodium is readily formed from aqueous alcoholic solutions of the reactants.[18] However, if acetone–water is used to dissolve the reactants little reaction is noted even after boiling for some time. However, on addition of a few drops of alcohol, the reaction goes quickly to completion. Again alcohol serves both as solvent and catalyst. We have also shown that even in this alcohol-catalysed reaction the addition of a little hypophosphorous acid or hydrazinium chloride greatly increases the rate.

The synthesis of the dichlorobiscyclohexanedionedioximatorhodium(III) anion cannot be achieved by boiling aqueous solutions of the ligand and rhodium trichloride, but on addition of alcohol the required product is quickly formed in solution.

Similarly the analogous bromide and iodide complexes of the bisdimethylglyoximatorhodium(III) moiety can be prepared by the catalysed reaction in aqueous solution of the $[RhX_6]^{3-}$ ion (made *in situ* by heating an aqueous solution of rhodium trichloride with excess of potassium bromide or iodide) with the alcoholic solution of the ligand. Substitution in the *trans*-dichlorobisdimethyldioximatorhodium(III) anion by other halides, except iodide, is slow even with hydridic catalysts present.

Although the formation of anionic compounds of the type $[Rh(DMGH)_2XCl]^-$ has been claimed [24] by refluxing the dichloro-compound with the ammonium salt of the anion, X^-, the sole product obtained in this work when such reactions were repeated has been the ammonium salt of the starting material $(NH_4)[Rh(DMGH)_2Cl_2]$. In particular, the infrared spectrum of the product when ammonium thiocyanate is refluxed with the dichloro-compound shows the absence of co-ordinated thiocyanate. We have been unable to prepare a pure thiocyanato-complex either by catalysed substitution in the $[Rh(DMGH)_2Cl_2]^-$ anion or by the catalysed action of dimethylglyoxime on $[Rh(SCN)_6]^{3-}$ anion.

It was claimed [17] that when dimethylglyoxime reacts with $[Rh\,py_4Cl_2]Cl$, chlorobisdimethylglyoximatopyridinerhodium(III) is formed. As discussed earlier, pyridine is indeed displaced, but the sole complex containing dimethylglyoxime produced is the dichlorobisdimethylglyoximatorhodate(III) ion, as its pyridinium or *trans*-dichlorotetrapyridinium(III) salts. Both $[Rh\,py_4Cl_2]^+$ and $[Rh(DMGH)_2Cl_2]^-$ react with reducing agents, and the presence of hydridic species has been demonstrated for both " reduced " complexes under certain conditions.[4,8] However, no combinations of solvent (water or ethanol), reducing agent, or temperature gave the desired compound, the most common product on allowing the reduced reaction mixture to oxidise being pyridinium dichlorobisdimethylglyoximatorhodate(III). It was finally found that when pyridinium dichlorobisdimethylglyoximatorhodate(III), suspended in hot pyridine, was heated with a little H_3PO_2, a clear solution forms, which rapidly deposits needle-like crystals of chlorobisdimethylglyoximatopyridinerhodium(III).

The best-known complex of rhodium(III) with dimethylglyoxime is that formulated [18] as " hydrogen dichlorobisdimethylglyoximatorhodate(III)." This formulation is undoubtedly correct in aqueous solution, as shown (Table 2) by the coincidence of the ultraviolet spectra of the monobasic acid and its salts. However, the formulation is incorrect for the solid state of the acid, since an O–H stretching mode is apparent at 3400 cm.$^{-1}$. This had been noted previously,[25] but not discussed. It leads to the formulation of the compound in the solid state as " dichloro(dimethylglyoximato)dimethylglyoximerhodium(III)," as in the analogous compound of cobalt(III).[26] This formulation is confirmed by (*a*) the shift of ν_{OH} to 2400 cm.$^{-1}$ on deuteration, giving $\nu_{OH} : \nu_{OD} = 1{\cdot}38$, and (*b*) the disappearance of ν_{OH} when the silver salt is formed. The hydrogen-bonded O–H · · · O frequency has been located in the original acid, and in its silver salt; in a strong mull, an extremely broad band occurs, centred at 2440 cm.$^{-1}$, which, in the acid, on deuteration (by several recrystallisations from heavy water) shifts; $\nu_{O-D\cdots O}$ occurs as a very broad, weak band centred at 1840 cm.$^{-1}$, giving $\nu_{O-H\cdots O} : \nu_{O-D\cdots O} = 1{\cdot}33$.

TABLE 1

Properties of isomers of $[Rh\,py_3(SCN)_3]$

Isomer	Colour	$\lambda_{max.}$	$\varepsilon_{max.}$	CH_2Cl_2	Infrared
1,2,3-	Yellow	372 [a]	1750	Insol.	853, 846, 838
1,2,6-	Orange	380 [b]	1650	Sol.	841

[a] In pyridine. [b] In dichloromethane.

TABLE 2

Electronic spectra of salts of the $[Rh(DMGH)_2Cl_2]^-$ anion (in water; λ in mμ)

Compound	λ	ε	λ	ε
" $H[Rh(DMGH)_2Cl_2]$ "	292	5×10^3	273	7×10^3
$(NH_4)[Rh(DMGH)_2Cl_2]$	292	5×10^3	273	7×10^3
$(GH)[Rh(DMG)H_2Cl_2]$ [a]	292	5×10^3	274	$7{\cdot}1 \times 10^3$

[a] (GH) = guanidinium.

---

[24] V. V. Lebedenski and I. A. Fedorov, *Ann. sect. Platine*, 1948, **21**, 157.
[25] H. Holtzclaw and J. P. Collman, *J. Amer. Chem. Soc.*, 1958, **80**, 2054.
[26] R. D. Gillard and G. Wilkinson, *J.*, 1963, 6041.

TABLE 3

Infrared spectra of dimethylglyoxime complexes of rhodium(III) (cm.$^{-1}$)

	"$H[Rh(DMGH)_2Cl_2]$"	$Ag[Rh(DMGH)_2Cl_2]$	$NH_4[Rh(DMGH)_2Cl_2]$	$[GH][Rh(DMGH)_2Cl_2]$ [a]	"HBr_2" [b]	"HI_2"
ν_{OH}	3400m	—	—	—	3280w	3300m
			3460	3410sh		
ν_{NH}	—	—	3246	3308s	—	—
			3135	3070sh		
ν_{CH}	—	2900w	2874w	—	—	—
ν_{OHO}	2440w, b	2480w, b	—	—	2420w	2400w
	—	—	—	—	—	—
				1660s		
ν_{NH_2}			1616	—	—	—
				1580w		
ν_{OH}	1600m, b	—	—	—	1598m	1598m
ν_{NO}	1508m	1515s	1520	1510s	1520w	1530m
ν_{CH} {	—	1420m	1424			
		1362m				
	1328m	1321m		1327m	1333w	—
	1240s	1241s	1245	1240s	1221s	1227s
	1129m	1129m	1124m	1124m	1121m	1121m
	1078s	1075s	1074s	1065s	1066s	1076s
ν_{OHX}?	1019w	—	—	—	1000m	1008w
	986w	—	977	997m	965m	970m
	—	—	—	880s, b	—	—
	860m, vb	—	—	—	842w	855wb
$\nu_{NH_4^+}$	—	—	839	—	—	—
	737s	733s	734s	732s	730w	728s

[a] GH = guanidinium. [b] " HBr " = $H[Rh(DMGH)_2Br_2]$. [c] " HI_2 " = $H[Rh(DMGH)_2I_2]$.

TABLE 4

Spectroscopic data for $[M(DMGH)_2pyCl]$ (M = Co or Rh)

Compound	$\nu_{O-H\cdot\cdot O}$	$\tau_{O-H\cdot\cdot O}$	τ_{py}		τ_{CH_3}	Ref.
			β	α		
$[Co(DMGH)_2pyCl]$	1710	−8·01	1·04 0·82 0·54	−1·11 −1·13	6·86	*a*
$[Rh(DMGH)_2pyCl]$......	2450	−2·05	2·67 2·55 2·46	1·49 1·38	6·76	*b*

[a] Gillard and Wilkinson, *J.*, 1963, 6041. [b] This work.

Infrared spectra for dihalogenobisdimethylglyoxime complexes with rhodium(III) are collected in Table 3. It is clear that all the solid dihalogeno-acids must be reformulated as $[Rh(DMGH)(DMGH)X_2]$. Although dichloro(dimethylglyoximato)dimethylglyoxime-rhodium(III) is fairly soluble in dimethylformamide, giving beautiful crystals by slow evaporation of the solution, no proton resonance signal due to an intramolecular hydrogen bond was observed in the solution, suggesting hydrogen transfer to give $Me_2NCONH_3^+$, *i.e.*, the dimethylglyoxime compound is a weaker base than dimethylformamide. It was further found that, for chlorobisdimethylglyoximatopyridinerhodium(III), the intramolecular hydrogen bond is by no means so obvious as that in analogous complexes of the first transition row. For example, in complexes of cobalt(III), the intramolecular hydrogen bond gives a resonance at $\tau \sim -8{\cdot}5$,[26] and in complexes of nickel(II), at $\tau \sim -8$.[27] Nor is the infrared absorption, *ca.* 1800 cm.$^{-1}$, found in the complexes of cobalt(III) observed; the corresponding absorption for the rhodium complex is at ~2400 cm.$^{-1}$. The spectroscopic properties of the cobalt(III) and rhodium(III) complexes are compared in Table 4.

The proton resonance due to O–H · · · O is observed at $\tau \sim -2$ in the rhodium(III) complex; its position varies slightly with dilution. Presumably, the hydrogen bond in the rhodium complex is longer and therefore weaker than that in the cobalt analogue, as a consequence of the larger radius of rhodium. The resonance spectrum due to the co-ordinated pyridine molecule is very similar to those observed in other complexes containing

[27] R. D. Gillard and J. E. Neale, unpublished work.

pyridine. In work using platinum(II) complexes, it was found[28] that the chemical shift of the β-protons of co-ordinated pyridine varied only very slightly from one square-planar complex to another. In this work, the chemical shifts of the β-protons are strikingly different in the octahedral cobalt(III) and rhodium(III) complexes, possibly owing to differences in π-bonding between pyridine and cobalt(III) or rhodium(III).

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College.

Electronic spectra were obtained using a Perkin-Elmer 350 spectrophotometer, proton resonance spectra using a Varian V-4311 spectrometer operating at 56·45 Mc./sec., infrared spectra (as mulls) using a Grubb–Parsons " Spectromaster " instrument. Conductivities were determined with a Mullard E7576 conductivity bridge, with a dipping cell.

trans-*Dichlorotetrapyridinerhodium*(III) *Chloride*.—Catalytic preparations were performed as follows: with hypophosphorous acid as described earlier;[4] in this work, sodium hypophosphite has been used equally effectively; with ethanol as described by Delépine.[1]

With zinc amalgam. Hydrated rhodium trichloride (0·26 g., 1 mmole) and pyridine (1 ml.) in methanol (7 ml.) were shaken in air, with 5% zinc amalgam (1 g.). Immediately, a pale yellow solution was formed, containing only the $[\mathrm{Rh\,py_4Cl_2}]^+$ ion, as shown by the spectral maximum at 410 mμ. The spent amalgam was removed, and the yellow solution was evaporated on a steam-bath, when needle-like crystals of *trans*-$[\mathrm{Rh\,py_4Cl_2}]\mathrm{Cl,5H_2O}$ were obtained, identified by infrared and electronic spectra (yield 0·58 g.; 94%).

With hydrazinium chloride. Hydrated rhodium trichloride (0·264 g., 1 mmole), sodium chloride (0·3 g.), and pyridine (1 ml.) in water (5 ml.) were heated; a warm, 10% aqueous, solution (0·1 ml.) of hydrazinium chloride was added, and an immediate colour change occurred. On cooling, yellow crystals (0·5 g.; 81%) of $[\mathrm{Rh\,py_4Cl_2}]\mathrm{Cl,5H_2O}$ were obtained.

With 2-methoxyethanol–ethanol. Hydrated rhodium trichloride (0·26 g., 1 mmole) in 1 : 1 2-methoxyethanol–ethanol (4 ml.) containing pyridine (1 ml.) was heated to boiling. Immediately, the solution became pale yellow; it was cooled, and treated with diethyl ether, whereupon *trans*-$[\mathrm{Rh\,py_4Cl_2}]\mathrm{Cl}$ was precipitated. This was collected, washed with ether, sucked dry, and recrystallised from water (yield 0·53 g.; 85%).

With hydridodichlorotris(triphenylphosphine)iridium(III). Rhodium trichloride (0·31 g., 0·5 mmole) in water (5 ml.) containing pyridine (2 ml.) was warmed to 50°, and a solution of hydridodichlorotris(triphenylphosphine)iridium(III) (0·005 g.) in pyridine (2 ml.) or acetone (3 ml.) added, and the resultant solution warmed slightly (to *ca.* 55°). In either case, the solution rapidly became pale yellow, showing the electronic spectrum of the *trans*-$[\mathrm{Rh\,py_4Cl_2}]^+$ cation, and, on cooling the solution in ice, crystals of *trans*-$[\mathrm{Rh\,py_4Cl_2}]\mathrm{Cl,5H_2O}$ were obtained, identified by electronic and infrared spectra (yield *ca.* 90%).

Reactions of the trans-*Dichlorotetrapyridinerhodium*(III) *Ion.*—*With bromide. trans*-Dichlorotetrapyridinerhodium(III) chloride pentahydrate (0·31 g., 0·5 mmole) in water (6 ml.) containing excess of potassium bromide (1 g.) was treated with hypophosphorous acid (0·5 ml.), and the mixture boiled. After 2 min. a fawn precipitate of the known[10] *trans*-dibromotetrapyridinerhodium(III) *trans*-tetrabromodipyridinerhodate(III) appeared. This was collected, washed with water, and dried *in vacuo* [Found: C, 30·7; H, 2·40; N, 7·3. Calc. for $\mathrm{C_{30}H_{30}Br_6N_6Rh_2}$: C, 30·8; H, 2·58; N, 7·18%] (yield 0·28 g.; 97%).

With iodide. trans-$[\mathrm{Rh\,py_4Cl_2}]\mathrm{Cl,5H_2O}$ (0·31 g., 0·5 mmole) in water (5 ml.) was treated with excess of potassium iodide (1 g.), the mixture (containing much crystallised $[\mathrm{Rh\,py_4Cl_2}]\mathrm{I}$) heated, and hypophosphorous acid (2 drops) added. The solution became clear, and then rapidly deposited a dark brown precipitate of 1,2,6-tri-iodotripyridinerhodium(III), identical with that formed[3] by removing co-ordinated pyridine from *trans*-di-iodotetrapyridinerhodium(III) iodide.

With ammonia. trans-$[\mathrm{Rh\,py_4Cl_2}]\mathrm{Cl,5H_2O}$ (0·31 g., 0·5 mmole) in aqueous 4N-ammonia (10 ml.) was heated till no further pyridine was evolved (*ca.* 3 min.). The yellow product, chloropentamminerhodium(III) chloride, was collected, and recrystallised from dilute hydrochloric acid (yield 0·13 g.; 87%). The product had (10^{-4}M in water) $\lambda_{\max.}$ 349 mμ, ε 100 (lit.,[29] $\lambda_{\max.}$ 349 mμ, ε 100).

[28] A. D. Westland and L. Westland, *Canad. J. Chem.*, 1961, **39**, 324.

[29] C. K. Jørgensen, *Acta Chem. Scand.*, 1965, **10**, 500.

With ethylenediamine. The directions of Meyer and Kienitz[11] for the reaction of *trans*-[Rh py$_4$Cl$_2$]Cl with ethylenediamine were followed, except that pyridine was removed on a steam-bath rather than at 120°. However, the compounds they described were probably mixtures, since, in this work, only white trisethylenediaminerhodium(III) chloride dihydrate was obtained (Found: C, 16·8; H, 5·8; N, 19·8. Calc. for $C_6H_{28}Cl_3N_6O_2Rh$: C, 16·9; H, 6·6; N, 19·7%); λ, 299 mμ, ε 101; λ, 253 mμ, ε 107 (lit.,[30] λ, 300 mμ, ε 100; λ, 253 mμ, ε 110). If insufficient ethylenediamine for complete reaction was used, then the yellow starting material could be recovered as well as the white [Rh en$_3$]Cl$_3$,2H$_2$O. This may explain the spurious earlier claim[11] that yellow "mixed" complexes such as [Rh enpy$_2$Cl$_2$]Cl may be obtained in this reaction.

With cyanide. Chlorodicyanobispyridinerhodium(III) *dihydrate. trans*-Dichlorotetrapyridinerhodium(III) chloride pentahydrate (0·616 g., 1 mmole) in water (25 ml.) was treated with an excess of potassium cyanide (0·65 g., 10 mmole). The yellow solution obtained on heating to *ca.* 80° gives crystals of *trans*-[Rh py$_4$Cl$_2$]Cl,5H$_2$O if allowed to cool. If the solution is boiled, pyridine is lost, and a yellow oil may appear briefly {possibly [Rh py$_3$(CN)$_2$Cl]} but in a few seconds redissolves, the solution subsequently precipitating *chlorodicyanobispyridinerhodium*(III) *dihydrate* (0·37 g.; 94%), which was washed with copious hot water, and dried *in vacuo* (Found: C, 37·5; H, 3·67; Cl, 8·8; N, 14·3; Rh, 29·3. $C_{12}H_{14}ClN_4O_2Rh$ requires C, 37·4; H, 3·64; Cl, 9·2; N, 14·5; Rh, 29·3%). The infrared spectrum showed bands (cm.$^{-1}$) at 3400s,b, 2201s, 2152s, 1631m,b, 1606s, 1480w, 1239m, 1217s, 1153s, 1071s, 1018s, 765s,b, and 693s,b. The compound was insoluble in all solvents such as alcohols, pyridine, dimethyl sulphoxide, etc.

Chloro-oxalatotripyridinerhodium(III).—This was made from *trans*-[Rh py$_4$Cl$_2$]Cl,5H$_2$O and potassium oxalate as described by Tchugaev.[16] The yellow needles were washed with hot water and dried *in vacuo* over silica gel (Found: C, 44·1; H, 3·38; Cl, 7·8; N, 8·9. Calc. for $C_{17}H_{15}ClN_3O_4Rh$: C, 44·0; H, 3·26; Cl, 7·6; N, 9·0%). The infrared spectrum showed bands (cm.$^{-1}$) at 1701s, 1680s, 1605m, 1241m, 1214m, 1157m, 1072s, 1016s, 855w, 801s, 780s, 766w, 724m, 710m, 699m, and 689s. The compound was slightly soluble in pyridine; it showed sharp m. p., decomposing *ca.* 200° to pyridine and a black residue.

Trithiocyanatotripyridinerhodium(III).—(a) *Uncatalysed, following the literature method.*[11] Rhodium trichloride trihydrate (0·26 g., 1 mmole) in water (10 ml.) was treated with potassium thiocyanate (1 g.) and the solution refluxed for 10 min. Pyridine (2 ml.) was added, and the mixture again refluxed for 10 min. The yellow solid which had formed was collected, washed with water, and dried at the pump. It is a mixture of the 1,2,3- and 1,2,6-isomers of [Rh py$_3$(SCN)$_2$] (Found: C, 42·1; H, 3·18; N, 16·51. Calc. for $C_{18}H_{15}N_6RhS_3$: C, 42·1; H, 2·94; N, 16·35%). It was taken up in dichloromethane (5 ml.) giving an orange solution (S) and a residual pale yellow solid, which was removed and washed with dichloromethane, the washings being discarded. The solid was recrystallised from aqueous pyridine (yield *ca.* 5%). It is 1,2,3-*trithiocyanatotripyridinerhodium*(III) (Found: C, 41·8; H, 3·40; N, 16·85. $C_{18}H_{15}N_6RhS_3$ requires C, 42·1; H, 2·94; N, 16·35%). The solution (S) was concentrated until crystals of 1,2,6-*trithiocyanatotripyridinerhodium*(III) were obtained; these were collected and recrystallised from ethanol, as orange-yellow plates (yield *ca.* 80%) (Found: C, 42·5; H, 2·95; N, 16·06%).

(b) *Catalysed.* The directions under (a) were followed except that a drop of hypophosphorous acid was added immediately after the pyridine, and the resultant mixture was boiled for 1 min. only. In this case, a little more of the pale yellow 1,2,3-isomer was obtained [Found (1,2,3-isomer): C, 42·4; H, 3·02; N, 16·5; (1,2,6-isomer): C, 41·7; H, 3·12; N, 16·6%]. The infrared spectra of the two isomers were as follows: 1,2,6-: 2079s, 1605m, 1302w, 1239w, 1215m, 1168sh, 1156m, 1062s, 1018m, 841m, 760s, and 691s: 1,2,3-: 2081s, 1603m, 1491sh, 1240w, 1216m, 1157m, 1064s, 1017m, 853sh, 846m, 838w, 768sh, 760s, 691sh, and 689s. The region normally concealed by the absorption due to Nujol (*ca.* 720 cm.$^{-1}$) was examined by preparing mulls in carbon disulphide as follows. The solid (*ca.* 0·004 g.) was ground with carbon disulphide (*ca.* 3 ml.) as usual. At an ambient temperature of 22°, the ground powder was nearly dry after 3 min. It was then rapidly transferred to a rock-salt plate, six drops of carbon disulphide were rapidly added, and a second rock-salt plate was immediately pressed on with a rotary motion, re-forming a mull. Without special precautions, this mull was sufficiently stable to give good spectra in the relevant region for about 10 min. After this, the solvent began to be lost from

[30] H. H. Schmidtke, Cyanamid European Research Institute, Report TIC-P 23, Geneva, 1963.

the centre of the mull as detected both by direct observation of dry powder, and by the apparently increased background absorption.

trans-*Dichlorotetrapyridinerhodium*(III) *Thiocyanate.*—As described by Meyer and Kienitz,[11] this was prepared for comparison purposes, by double decomposition. The infrared spectrum showed bands (cm.$^{-1}$) at: 2060s, 1601m, 1211m, 1157m, 1073m, 1061m, 1016m, 772sh, 768s, 751m, 737m, 708m, 697s, and 689s.

trans-*Dihalogenobisbipyridylrhodium*(III) *Salts.*—Electronic spectra, measured in aqueous solution (*ca.* 10^{-3}M for the visible region and *ca.* 10^{-5}M for the ultraviolet) are in Table 5. Infrared spectra, taken on mulls, are in Table 6.

TABLE 5

Electronic spectra of *trans*-$[Rh(AA)_2X_2]^+$ salts (AA = bipy or 1,10-phenanthroline; λ in mμ)

Compound	λ	ε	λ	ε	λ	ε	λ	ε
$[Rh(bipy)_2Cl_2]^{+}$ [a]	383	110	312	$1{\cdot}2 \times 10^4$	301	$9{\cdot}8 \times 10^3$	—	—
,, [b]	384	112	312	$1{\cdot}1 \times 10^4$	301	$9{\cdot}3 \times 10^3$	—	—
$[Rh(bipy)_2Br_2]^+$	395	415	311	$2{\cdot}7 \times 10^4$	302	$2{\cdot}25 \times 10^4$	—	—
$[Rh(bipy)_2I_2]^+$	402	1400	312	$2{\cdot}4 \times 10^4$	301	$2{\cdot}25 \times 10^4$	238	7×10^4
$[Rh(o\text{-}phen)_2Cl_2]^+$......	385	110	350	$2{\cdot}5 \times 10^3$	333	$2{\cdot}6 \times 10^3$	318sh	$4{\cdot}1 \times 10^3$
					300sh	$1{\cdot}3 \times 10^4$	272	$5{\cdot}6 \times 10^4$

[a] Prepared following Martin and Waind, *J.*, 1958, 4284. [b] Catalytically prepared.

TABLE 6

Infrared spectra of $[Rh(bipy)_2X_2]X,2H_2O$

X = Cl [a]	Cl [b]	Br	I [c]	X = Cl [a]	Cl [b]	Br	I [c]
3400s, b	3410s, b	3350m, b	—	1063w	1064sh	1063w	1062w
1651m, b	1650m, b	1647w, b	—	1045w	1046sh	1046w	—
1608s	1608s	1601s	1601m	1040m	1040m	1040m	1036m
1493sh	1493sh	1492w	1495w	1028m	1029m	1028w	1029w
1315w	1316w	1316m	1309m	968	969w	970w	972m
1280w	—	1280w		898m	899w	901m	895w
1244m	1244m	1243m	1241w			893sh	
		1173sh	1170	805w	—	805w	803w
1160s	1160m	1164sh		778s		780sh	778sh
		1158s	1159m		772s	773s	771sh
1106m	1106w	1106m	1105m	769s		768sh	767s
1078m	1077m	1079m	1074m	729s	729s	729s	728s

[a] As nitrate, prepn. (1); nitrate bands occurred at 1350sb and 832m. [b] As chloride, prepn. (2)—(6). [c] Anhydrous.

trans-*Dichlorobisbipyridylrhodium*(III) *salts.* (1) The nitrate was prepared by the more recent literature method,[20] fusion of rhodium trichloride and bipyridyl, and recrystallisation of the nitrate. We find it to be a dihydrate. (2) The chloride was prepared by a modification of an earlier literature method;[19] rhodium trichloride trihydrate (0·26 g., 1 mmole) in ethanol (5 ml.) was treated while hot with bipyridyl (0·343 g., 2·2 mmole) in ethanol (5 ml.). The mixture was heated, when the colour changed (*ca.* 3 min.) from red to yellow. At this stage, on cooling, crystals of $[Rh(bipy)_2Cl_2]Cl,2H_2O$ were obtained, which were recrystallised from water (yield 0·5 g.; 89%) (Found: C, 42·4; H, 3·53; N, 9·6. Calc. for $C_{20}H_{20}Cl_3N_4O_2Rh$: C, 43·0; H, 3·61; N, 10·0%).

This preparation was repeated with acetone in place of ethanol. The red colour of the original mixture lightened only very slowly. However, on addition of ethanol (2 ml.), the colour changed to yellow during 1 min., and the desired $[Rh(bipy)_2Cl_2]Cl,2H_2O$ was obtained.

The preparation was repeated in 1 : 1 ethanol–2-methoxyethanol. Immediately on ebullition, the desired complex (anhydrous) began to precipitate, and, on cooling, it was recovered in 93% yield. It could be dissolved in hot water and the sparingly soluble nitrate or perchlorate salts obtained by treating the hot solution with a concentrated solution of sodium nitrate or perchlorate. The nitrate dihydrate (Found: C, 41·0; H, 3·65; N, 11·8. Calc. for $C_{20}H_{20}Cl_2N_5O_5Rh$: C, 41·1; H, 3·45; N, 12·0%) was identical with that prepared by method (1) above. The perchlorate (Found: C, 40·1; H, 2·99. Calc. for $C_{20}H_{16}Cl_3N_4O_4Rh$: C, 40·0; H, 2·72%) was identical with the literature product.[20] (3) With hydrazine as catalyst: rhodium trichloride trihydrate (0·26 g., 1 mmole) in water (5 ml.) was treated with bipyridyl (0·34 g., 2·2 mmole) in warm ethanol (5 ml.) and the mixture heated; to the hot mixture (60°), hydrazinium chloride (0·02 g.) was added, and the mixture brought to boiling. Immediately, the mixture gave a clear yellow solution, which, on cooling, deposited the desired complex as small yellow needles (0·48 g.; 87%). (4) Using hypophosphorous acid: the preparation was performed as described under (3), except that hypophosphorous acid (0·05 ml.) was added in place of hydrazinium chloride. Again, immediate formation of [Rh bipy$_2$Cl$_2$]Cl occurred, which was collected after cooling and recrystallised from water.

With larger amounts of hypophosphorous acid present, the reaction took a different course; rhodium trichloride trihydrate (0·26 g., 1 mmole) in water (5 ml.) was mixed with bipyridyl (0·34 g., 2·2 mmole) in ethanol (5 ml.), and the mixture kept at 60° while hypophosphorous acid (1 ml.) was added. A clear yellow solution at once resulted; this was heated briefly to boiling, when it became brown. On cooling (even in the absence of air) yellow crystals are formed (0·53 g.). Phosphorus was present, but chlorine absent. The infrared spectrum showed bands at 3380m,b, 2350m (PH), 1650w,b, 1605m, 1311m, 1248m, 1161m, 1139sh, 1126sh, 1113sh, 1075w, 890s,vb (PO), 773s, and 729s cm.$^{-1}$. The compound can be recovered apparently unchanged from hot hydrochloric acid. When the yellow crystals are heated with water, a brown solution was formed, which rapidly became yellow; at this stage a definite high-field line was observed in the n.m.r. spectrum, at 1130 c./sec. relative to H_2O, showing the presence of an Rh–H bond. On cooling and standing, pale yellow crystals are formed, apparently identical with those above.

Exactly similar behaviour was observed with the analogous *o*-phenanthroline complex, and it is relevant that when dichlorobispyridylrhodium(III) chloride was treated in aqueous solution with sodium hypophosphite, the product after heating is apparently identical with that from rhodium trichloride and bipyridyl described above.

Dibromo-salt. When solutions of $[RhBr_6]^{3-}$ in water and bipyridyl in ethanol are mixed, a fawn precipitate is at once obtained; this is formulated Rh$_2$bipy$_3$Br$_6$ (Found: C, 31·0; H, 2·52; N, 7·3. Calc. for $C_{30}H_{24}Br_6N_6Rh_2$: C, 31·2; H, 2·08; N, 7·3%). However, the desired salt was obtained as follows: rhodium trichloride trihydrate (0·26 g., 1 mmole) in aqueous solution (10 ml.) was heated with excess of potassium bromide (1·0 g.); the solution was boiled for 2 min., then bipyridyl (0·34 g., 2·2 mmole) in hot alcohol (6 ml.) was added to the hot aqueous solution (60°). 0·02 g. of hydrazinium chloride was added and the mixture brought to boiling. The solution rapidly changed colour and a little fawn precipitate was given immediately. The solution was filtered when hot and allowed to cool slowly to crystallise. The *salt trans*-[Rh dipy$_2$Br$_2$]Br,2H$_2$O was collected as orange plate-like crystals (yield 0·58 g.; 84%) (Found: C, 35·0; H, 3·29; Br, 35·6. $C_{20}H_{20}Br_3N_4O_2Rh$ requires C, 34·8; H, 2·92; Br, 34·8%).

Di-iodo-salt. trans-Dichlorobisbipyridylrhodium(III) chloride dihydrate (0·28 g., 0·5 mmole) was dissolved in hot water (8 ml.) and a solution of potassium iodide (0·33 g., 2 mmole) in water (2 ml.) was added. To the hot mixture hypophosphorous acid (0·02 ml.) was added and the solution brought to boiling. A rapid deepening in colour was noted and *trans*-di-iodobisbipyridylrhodium(III) iodide crystallised as a brick-red solid. It was collected after cooling, washed with cold water, then ethanol, and air-dried (yield 0·36 g.; 90%) (Found: C, 29·9; H, 2·50; N, 7·11. $C_{20}H_{16}N_4I_3Rh$ requires C, 30·2; H, 2·03; H, 7·04%).

trans-*Dichlorobis*-1,10-*phenanthrolinerhodium*(III) *Chloride Dihydrate*.—Rhodium trichloride trihydrate (0·26 g., 1 mmole) in water (5 ml.) was mixed with 1,10-phenanthroline (0·4 g., 2·2 mmole) in warm alcohol (7 ml.), and the mixture heated to 60°. Hydrazinium chloride (0·02 g.) was added and the mixture brought to boiling. Immediately, the mixture gave a clear yellow solution which, on cooling, deposited the desired *complex* as its dihydrate, which was recrystallised from water (Found: C, 47·1; H, 3·62; N, 18·0. $C_{24}H_{20}Cl_3N_4O_2Rh$ requires C, 47·6; H, 3·33; N, 17·6%). The infrared spectrum showed bands (cm.$^{-1}$) at 3400s,b, 1632m,b, 1601m, 1582m, 1501m, 1336w, 1301w, 1218w, 1201w, 1140m, 1102w, 1083w, 1027m, 880w, 850s, 749m, 729m, and 719s.

Trisethylenediaminerhodium(III) *Chloride Dihydrate*.—Hydrated rhodium trichloride (0·26 g., 1 mmole) in ethanol (5 ml.) at 60° was treated with ethylenediamine hydrate (1 ml.) in ethanol (5 ml.), when a white precipitate immediately formed, which was collected, washed with ethanol, and dried (0·36 g.). It was recrystallised from hot water–ethanol as the dihydrate (Found: C, 16·7; H, 6·8; N, 19·9. Calc. for $C_6H_{28}Cl_3N_6O_2Rh$: C, 16·9; H, 6·6; N, 19·7%).

Trispropylenediaminerhodium(III) *Chloride*.—In the same way as for the ethylenediamine complex, trispropylenediaminerhodium(III) chloride hydrate was obtained as white crystals (Found: C, 24·4; H, 6·96. Calc. for $C_9H_{32}Cl_3N_6ORh$: C, 24·05; H, 7·15%).

trans-*Dichloro*(*dimethylglyoximato*)*dimethylglyoximerhodium*(III).—This was prepared by the literature method,[18] and recrystallised from copious hot water (Found: Cl, 18·3. Calc. for $C_8H_{15}Cl_2N_4O_4Rh$: Cl, 18·2%). In addition to the bands given in Table 2, a band with λ 345, ε 1130 was observed in aqueous solution ($\sim 10^{-3}$M). The ammonium,[31] guanidinium,[31] and silver [18] salts were prepared by literature methods.

Deuteration.—The complex $[Rh(DMGH_2)(DMGH)Cl_2]$ (0·1 g.) was suspended in deuterium oxide (3 ml.) and the suspension refluxed for 15 min., then filtered hot. On cooling the filtrate, yellow crystals were obtained which, from their infrared spectrum, were almost completely deuterated $[Rh(Dd_2)(Dd)Cl_2]$, where Dd_2 and Dd represent deuterated dimethylglyoxime and its anion, respectively.

trans-*Dichloro*(*cyclohexanedioximato*)*cyclohexanedioximerhodium*(III).—Rhodium trichloride trihydrate (0·2 g.) in water (1 ml.) and ethanol (9 ml.) was treated with cyclohexane-1,2-dionedioxime (0·3 g.) in ethanol (10 ml.). The mixture was boiled for 1 min., then cooled rapidly, whereupon yellow *crystals* appeared. These were collected, and recrystallised from copious hot water (yield 0·2 g.) (Found: C, 31·5; H, 4·3; N, 12·5. $C_{12}H_{18}Cl_2N_4O_4Rh$ requires C, 31·6; H, 3·9; N, 12·3%). The compound, though soluble in alcohol, reacts rapidly with it when hot. Its infrared spectrum shows bands (cm.$^{-1}$) at 3215s, 1611m, 1572m, 1511s, 1340m, 1305m, 1252w, 1227s, 1047s, 978s, 932w, 915m, 810m, and 751m. When treated with sodium borohydride in water–ethanol (1 : 10), a very insoluble blue compound is obtained, analogous to the reaction [22] for the bisbipyridyl compound, and for other complexes of rhodium(III) of the type $[Rh(AA)_2Cl_2]^{\pm n}$, where AA is a chelating, π-bonding, nitrogenous ligand, such as 1,10-phenanthroline or dimethylglyoxime. Such blue compounds are, in fact, markedly red-blue dichroic, and we now attribute this, and their marked insolubility, to the presence of a columnar structure based on rhodium–rhodium bonds, the rhodium being present, formally, as Rh^I, with the d^8 electronic configuration. The analogy with the well-known structure of the isoelectronic species bisdimethylglyoximatonickel(II) is obvious.

Substitution Reactions.—*With thiocyanate*. According to the literature,[24] when $[Rh(DMGH)_2Cl_2]^-$ is refluxed in aqueous solution with an excess of ammonium thiocyanate, the product is $NH_4[Rh(DMGH)_2(SCN)Cl]$. This reaction was repeated, but the yellow-brown crystals obtained were actually $(NH_4)[Rh(DMGH)_2Cl_2]$, identified by analysis and the identity of the infrared spectrum with that of an authentic sample; in particular, no absorption due to the thiocyanate group was found (Found: C, 22·7; H, 4·35; Cl, 17·1. Calc. for $C_8H_{18}Cl_2N_5O_2Rh$: C, 22·8; H, 4·26; Cl, 16·8%). Bands occur (cm.$^{-1}$) at 3120, 2610w,b, 2100w,b, 1848w,b, 1656w,b, 1520, 1235s, 1118s, 1074s, 998w, 976m, 840m, and 733s. When the product was warmed (70°) with 1 : 1 hydrochloric acid, crystals of the original $[Rh(DMGH)(DMGH)Cl_2]$ were obtained. When the preparation was repeated in the presence of hypophosphorous acid, once again the original dichloro-compound was recovered unchanged.

Chlorobisdimethylglyoximatopyridinerhodium(III). (1) When $[Rh(DMGH_2)(DMEH)Cl_2]$ is refluxed with pyridine, the beautiful light brown crystals obtained are the pyridinium salt [18] $(pyH)[Rh(DMGH)_2Cl_2]$, and, again, on treatment with hydrochloric acid, $[Rh(DMGH_2)(DMGH)Cl_2]$ is regenerated. Authentic pyridinium *trans*-dichlorobisdimethylglyoximatorhodate(III), originally described by Dwyer and Nyholm,[18] is very readily prepared by allowing a cold solution of $[Rh(DMGH_2)(DMGH)Cl_2]$ in pyridine to stand. After 14 days, the large brown crystals of the desired compound were collected (Found: C, 32·8; H, 4·2; N, 14·9. $C_{13}H_{20}Cl_2N_5O_4Rh$ requires C, 32·2; H, 4·1; N, 14·5%).

(2) The literature method [17] using the reaction of *trans*-dichlorotetrapyridinerhodium(III) chloride with dimethylglyoxime during 36 hr. in refluxing water was re-examined. The product, however, was not the desired compound, but a mixture of yellow-orange 1,2,3-trichlorotripyridinerhodium(III) (Found: C, 39·9; H, 3·62; N, 9·45. Calc. for $C_{15}H_{15}Cl_3N_3Rh$: C, 40·3; H, 3·35; N, 9·40%) (λ 407 mμ, ε 138. Lit.,[9] λ 407 mμ, ε 140) and a pale yellow powder (*ca.* 5—10% of the whole) insoluble in dichloromethane. This by-product contains rhodium, chlorine and, from its infrared spectrum, pyridine, but no dimethylglyoxime: bands occur at 1606, 1311, 1220, 1177, 1161, 1074, 1023, 770, and 698 cm.$^{-1}$. Analytical data are inconclusive.

It is noteworthy that after refluxing the original mixture for 3 hr., the components could

[31] L. Tchugaev and V. V. Lebendenski, *Z. anorg. Chem.*, 1913, **83**, 1.

very readily be separated by virtue of the insolubility of dimethylglyoxime in water. No reaction appeared to have occurred at this stage, since the electronic spectrum of the soluble material showed it to be pure *trans*-dichlorotetrapyridinerhodium(III) cation.

(3) The literature method [17] was modified in several ways: (*a*) [Rh py_4Cl_2]Cl,$5H_2O$ (0·31 g., 0·5 mmole) and dimethylglyoxime (0·06 g., 0·5 mmole) in warm ethanol (6 ml.) were treated with sodium borohydride (0·01 g.) in water (1 ml.). Pyridine was at once evolved; the solution was concentrated to 3 ml. and allowed to cool, when the *salt trans*-[Rh py_4Cl_2] *trans*-[Rh(DMGH)$_2$Cl$_2$] (0·30 g.) crystallised (Found: C, 37·3; H, 4·0; N, 11·8. $C_{28}H_{34}Cl_4N_8O_4Rh_2$ requires C, 37·6; H, 3·8; N, 12·5%).

(*b*) [Rh py_4Cl_2]Cl,$5H_2O$ (0·31 g., 0·5 mmole) and dimethylglyoxime (0·14 g., 1·2 mmole) in warm ethanol (7 ml.) were treated with sodium borohydride (0·1 g.) in water (1 ml.). Pyridine was lost, and, on concentrating the solution to half its bulk, yellow crystals of pyridinium *trans*-dichlorobisdimethylglyoximatorhodate(III) were obtained (Found: C, 32·7; H, 4·16; N, 15·1. Calc. for $C_{13}H_{19}Cl_2N_5O_4Rh$: C, 32·2; H, 4·13; N, 14·5%). In the absence of catalysts other than ethanol this salt was also the reaction product.

(*c*) The components as in (*b*) were heated in 2-methoxyethanol (50 ml.) on a steam-bath, the solution being evaporated to dryness. The resultant yellow solid was dissolved in warm water, the solution was filtered, and, on cooling the filtrate, yellow crystals were obtained of pyridinium *trans*-dichlorobisdimethylglyoximatorhodate(III) (Found: C, 31·7; H, 4·26; N, 14·2).

(*d*) When [Rh(DMGH$_2$)(DMGH)Cl$_2$] is treated either in aqueous or ethanolic solution with sodium borohydride, a blue solid is obtained. This was allowed to re-oxidise in the presence of pyridine, but the sole product was pyridinium dichlorobisdimethylglyoximatorhodate(III). When hypophosphorous acid was used in the place of sodium borohydride, in aqueous-ethanolic media, the original acid was recovered unchanged.

(4) *Chlorobisdimethylglyoximatopyridinerhodium*(III). A hot suspension of dichloro(dimethylglyoximato)dimethylglyoximerhodium(III) (0·41 g., 1 mmole) in hot pyridine (5 ml.) was treated with hypophosphorous acid (0·1 ml.). The excess of solid at once dissolved, and on cooling the clear yellow solution acicular crystals of the desired *compound* were obtained, which were collected, washed with ice–water, and recrystallised from dichloromethane (yield 0·40 g.; 89%) (Found: C, 35·45; H, 4·13; N, 15·8; Cl, 8·25. $C_{13}H_{19}ClN_5O_4Rh$ requires C, 34·87; H, 4·28; N, 15·6; Cl, 7·92%). The infrared spectrum shows bands (cm.$^{-1}$) at ~2500s,b, 1608s, 1561sh, 1519s, 1337m, 1261s, 1221m, 1150s, 1140sh, 1078s, 1069s, 1021m, 1004w, 980s, 848m, 780s, 739s, and 701s.

trans-*Dibromo*(*dimethylglyoximato*)*dimethylglyoximerhodium*(III).—Rhodium trichloride (0·26 g.) in aqueous solution (10 ml.) was treated with excess of potassium bromide (1·0 g.); the solution was boiled for 2 min., then dimethylglyoxime (0·2 g.) in hot ethanol (4 ml.) was added. The mixture was heated, with or without the addition of a small amount (1 drop) of hypophosphorous acid. In the absence of hypophosphorous acid, during about 2 min., the colour of the solution gradually fades, and crystals of the desired compound begin to appear. If hypophosphorous acid is added, there is almost immediately a rapid change of colour, and, if the solution is cooled at this stage, *trans*-dibromo(dimethylglyoximato)dimethylglyoximerhodium(III) crystallises in very good yield (Found: C, 20·1; H, 3·36; N, 11·7. Calc. for $C_8H_{15}Br_2N_4O_4Rh$: C, 19·8; H, 3·0; N, 11·3%). The electronic spectrum in aqueous solution (~10^{-3}M for visible, ~5×10^{-5}M for ultraviolet) showed bands at 435 mμ (sh), ε 80; λ 335 mμ, ε $5·8 \times 10^3$; λ, 264 mμ, ε $1·9 \times 10^4$.

Strangely, dichloro(dimethylglyoximato)dimethylglyoximerhodium(III) can be recovered unchanged after refluxing for 5 min. in an aqueous solution containing excess of potassium bromide and hypophosphorous acid.

Di-iodo(*dimethylglyoximato*)*dimethylglyoximerhodium*(III).—(1) Rhodium trichloride (0·26 g.) in water (10 ml.) containing potassium iodide (1·6 g.) was boiled for 2 min., and the extremely dark solution produced was mixed with dimethylglyoxime (1·4 g.) in ethanol (5 ml.) and the mixture heated. Unlike the analogous bromo-system, no crystals were so obtained, dark brown polymer being formed. However, if a drop of hypophosphorous acid was added to the hot reaction mixture, a change of colour occurred, and, on cooling, the desired compound appeared as orange-brown, glistening, acicular *crystals* (0·53 g.) (Found: C, 16·8; H, 2·98; I, 43·0. $C_8H_{15}I_2N_4O_4Rh$ requires C, 16·3; H, 2·54; I, 43·05%).

(2) Dichloro(dimethylglyoximato)dimethylglyoximerhodium(III) (0·4 g., 1 mmole) in water (10 ml.) containing excess of potassium iodide (1·0 g.) was heated, and, while hot, treated with

hypophosphorous acid (1 drop). The clear yellow solution at once became orange, and, on cooling, orange-brown needles (0·5 g.; 85%) of dio-iodo(dimethylglyoximate)dimethylglyoxime-rhodium(III) were obtained (Found: C, 16·5; H, 3·01; N, 9·72%). The electronic spectrum in water (10^{-3}M for visible, 10^{-5}M for ultraviolet) shows bands at 450 mμ (sh), ε 135; 335 mμ, ε 1·25 × 10^4; 264 mμ, ε 4 × 10^4.

trans-*Bisdimethylglyoximatodiamminerhodium*(III) *Chloride Pentahydrate*.—This is a modification of the method of Tchugaev and Lebedinski:[31] chloropentamminerhodium(III) chloride (0·56 g.), dimethylglyoxime (0·66 g.), ammonium acetate (1·2 g.), and water (14 ml.) were heated overnight at 150° in a sealed tube. After cooling, the solution was filtered to remove unchanged dimethylglyoxime (0·085 g., m. p. 240°) and the filtrate evaporated to dryness. The yellow product (0·6 g.) was recrystallised from water, collected, washed with a little ice–water, and dried in air at 100° (Found: C, 18·9; H, 5·8; N, 16·6. Calc. for $C_8H_{30}ClN_6O_9Rh$: C, 19·5; H, 6·1; N, 17·0%); Λ, 122 mhos (10^{-3}M in water). The electronic spectrum (3·1 × 10^{-3}M in water) had λ 335, ε 2·1 × 10^3; λ 266, ε 1·2 × 10^4.

We thank Johnson, Matthey and Co. Ltd. for the loan of rhodium and E. I. du Pont de Nemours and Co. for financial support (J. A. O.).

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON S.W.7.

[*Received, June* 18*th*, 1964.]